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Review of biodiesel synthesis from waste oil under elevated pressure and temperature: Phase equilibrium, reaction kinetics, process design and techno-economic study

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ABSTRACT

The synthesis of biodiesel under elevated pressure and temperature could be promising technology which could result in sustainable biodiesel production, from renewable and waste streams like waste oil or used frying oil, thereby having no impact on biodiversity and the environment. This paper is comprehensive review of biodiesel synthesis from waste oil under elevated pressure and temperature: the supercritical or subcritical conditions of alcohol, with or without the use of heterogeneous catalyst. The review compromises the thermodynamic data, phase equilibria, phase composition and distribution during reaction, kinetic parameters and kinetic modeling, are presented. This type of data is necessary for process design and optimization. Process economics is analyzed and the impact of different production parameters (feedstock type, process parameters as temperature, pressure and alcohol to oil ratio, and different technology) is summarized and discussed.

Contents

1. Introduction

Biodiesel, defined as a mixture of monoalkyl esters of long chain fatty acids (mainly the fatty acid methyl (ethyl) esters or FAME (FAEE)) derived from a renewable lipid feedstock, such as vegetable oil or animal fat, is most commonly used renewable biofuel for internal combustion engines. The main advantage of the application of biodiesel fuel in the internal combustion engines is better quality exhaust gas emissions and the fact that it does not contribute to a rise in the level of carbon dioxide in the atmosphere. In addition, biodiesel has a relatively high flash point

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(average value of 150 °C), which makes it easier for handling, transport and storage and its biodegradability contribute to environmental safety. However, the most important advantage of biodiesel fuel is its production from renewable sources and its contribution to the sustainable energy supply [1,2]. Although a large-scale production of biofuels could cause biodiversity loss, conflicts with food security and increasing of net greenhouse gas emissions, small-scale production of biofuels have been concerns about the sustainability.

The International Energy Agency predicts that biofuels will provide approximately 27% of the world transport fuel by 2050 but currently biofuels provide only 2% of total transport fuel. These estimates are an integral part of current energy strategies for both developing and industrialized countries aiming to provide future abundant, cheap, renewable and environmentally friendly energy source [3]. In their report, Webb and Coates underline an important question: Even though much of the literature on biofuels implicitly assumes that biofuel is “renewable energy” and therefore an objective in itself, the issue is however, how does biofuel perform when compared to other renewable energy sources [4]? If a comparison between different renewable energy options is done in terms of arable land required to drive 100 km, the following results would indicate a striking differences between options: wind energy requires 1 m^2 of land, and hydrogen from lignocelluloses requires 5.3 m^2, while rapeseed biodiesel requires 53.6 m^2 [4]. Obviously, it appears that conventional biofuels offer some of the least land-efficient renewable energy sources [4].

Sustainability criteria and standards have already been integrated into certain voluntary certification schemes as well as national mandatory regulations, in order to prop-up sustainable biofuels. However, gaps in sustainability criteria and standards include cross-over effects with food sector, as well as environmental and social impacts. Further development and refinement of criteria is needed in order to have all possible relevant impacts properly evaluated, based on full life-cycle analysis (LCA). Most research results support approaches which improve the sustainability of agriculture as a whole, and not by sub-sector. Additionally, LCA′s of biofuels have to be improved and should take into account a broad range of assessment impacts along the life-cycle (farming, different feedstocks, and land use; techniques and practices; tailpipe emissions and consequences; biodiversity and more) [4,5].

Policy discussions over biodiesel and generally biofuels in industrially developed nations during 2012 have shown the increasing complexity of the topic. Originally promoted as a way of decreasing dependence on fossil fuels (from the perspective of oil importing countries) and avoiding the carbon emissions generated by them, biodiesel production has now been widely recognized to have strong impact on agricultural markets and even land-use patterns. Still high uncertainty that still remains over the impact of biofuels on food security and the environment, has made decision making complex and, in some cases, controversial. The optimal use of land, water and other resources depends on a country′s specific conditions and prioritized policy objectives. The development of biofuels in developing nations has been largely driven by Governments, through fiscal measures, subsidies and various other incentives, including trade policies. These measures have come under considerable scrutiny as they have resulted in debatable achievements. These incentives also usually fail to promote sustainability but they could be optimized to yield more positive outcomes. Financial support for biofuels that generate less environmental impact and less greenhouse gas emissions should be obviously prioritized, while focus of research and development of biofuels should target wastes and residues as primary feedstock [4].

Beside other limitation, the main obstacle for wider application of biodiesel is its relatively high cost. This is still the truth, although the price gap between petroleum based diesel fuel and biodiesel is narrowing due to the recent almost drastic changes of crude oil price (at the beginning of 2008–$150/bbl, the end of 2009–$40/bbl and the end of last year to $100–110/bbl). Such unstable price market of crude oil could be also expected in forthcoming years with tendency, as pointed out by many analyses at the end of 2012, to be very close to $250/bbl. This fact also requires that the overall cost of biodiesel fuel production needs to be reduced either by the reduction of raw material cost (vegetable oil, animal fat, and used vegetable oil), by decrease of utilities consumption (energy) and, of course, the application of more efficient processing technology taking into account its impact on the environment [6].

Waste cooking oil as cheep feedstock is produced around the world and developed countries produce million gallons of waste cooking oil per day. The large amounts of waste cooking oils are illegally dumped into rivers and landfills causing environmental pollution. The energy information administration in the United States estimated that around 100 million gallons of waste cooking oil is produced per day in USA. The per capita waste cooking oil production in Canada is approx. 9 pounds per year. In the EU countries, the total waste cooking oil production is approximately 700,000–1,000,000 t/year. The UK produces over 200,000 t of waste cooking oil per year. These quantities are sufficient for sustainable production of biodiesel if the collecting supply chain of waste cooking oil is operational [4,6,7].

The synthesis of biodiesel represents challenge for many researchers in the World requesting as main task determination the most economical and at the same time environmentally acceptable technology of production. Synthesis can be accomplished using several different technologies, therefore the selection of the most economical and at the same time environmentally acceptable production technology requires deep understanding of the underlying process phenomena. Application of supercritical alcohols (methanol and ethanol) for biodiesel production seems to be a potential solution which might fulfill both tasks [1,2,7,8]. The process does not require presence of a homogeneous or heterogeneous catalyst and proceeds at a very high rate. Moreover, the subsequent separation and purification steps are far simpler than in any other biodiesel processing technology. Subcritical transesterification is a promising method for a more environmentally friendly biodiesel production as a result of its feedstock flexibility, production efficiency and environmentally friendly benefits. Moreover, decreasing temperature and pressure, synthesis under subcritical conditions but with the aid of heterogeneous catalyst could also be the desirable technology for biodiesel production. The detailed techno-economic analysis was performed and will be underlined in this paper with comparison to conventional production.

The production of biodiesel fully compliant with EN 14214:2012 or ASTM 6751-12 is a very challenging task. To meet the both standards biodiesel should to have maximum 0.7% of glycerides and glycerol. Unconverted triglycerides, diglycerides, monoglycerides and glycerol, water and the other undesired components could cause significant engine damage and power loss. Therefore, the high conversion and purification steps are the most important for biodiesel production [9]. Regarding all this facts, and facts from previously published data, the synthesis of biodiesel under elevated pressure and temperature could be the only promising technology which could produce biodiesel in a sustainable way using renewable material from waste streams (from waste oil), thereby not impacting the biodiversity nor the environment in a negative way.

The aim of this paper is to summarize and to give comprehensive review of biodiesel synthesis from waste oil under elevated

pressure and temperature: the supercritical or subcritical conditions (of alcohol) with or without use of heterogeneous catalyst. The paper gives the detailed process design which compromises the thermodynamic data, phase equilibria, phase composition and distribution during reaction, kinetic data and kinetic modeling. All this data are necessary for process optimization and control. Moreover, techno-economic study was analyzed and impacts of different production parameters (feedstock, process parameters as temperature, pressure and alcohol to oil ratio and different technology) are summarized and discussed.

2. Process design

2.1. Phase equilibria and component distribution in reactor

The analysis of phase equilibria during synthesis of methyl or ethyl esters of fatty acids (FAME or FAEE) at high pressure and temperature is very important for describing the kinetic of process. Diglycerides and monoglycerides formed during methanolysis of triglycerides, together with FAME and glycerol which are the final products of reaction, make this system very complex for the phase transition analysis. The production of biodiesel at temperature and pressure near or above the critical values of the alcohols (subcritical and supercritical alcoholysis) has been in focus recently since it has the potential to solve problems associated with input material quality and process robustness. Thus, the knowledge of phase equilibria under various (medium and high) pressures, and over wide range of temperature, for systems with substantial excess of methanol (molar ratio of alcohol to oil=40–42:1), is an obvious goal for further process development, detailed design and optimization. Furthermore, the existence of one pseudo homogeneous phase is crucial for obtaining a high reaction rate between an alcohol and triglycerides (without use of a catalyst) which could be realized under subcritical or supercritical condition [1,10–22].

Methanolysis or ethanolysis of triglycerides and synthesis of biodiesel is complex reaction which can be represented as parallel and consecutive complex kinetics consisting of three second order reversible reactions [13–16]. The composition of reaction mixture at the end of synthesis comprises mainly the products: methyl or ethyl esters (biodiesel), the small amount of glycerol (up to 5 mass %), and the large excess of alcohol. Monoglycerides and diglycerides are formed as intermediate products and could be present only in traces. This process realized under subcritical or supercritical conditions for methanol shows complex phase behavior [11,12].

Phase equilibrium of methyl esters, methanol, glycerol or monoglycerides (two or three component) at moderate temperature and pressure was the subject of research from several papers published recently [17–26] and a review published by Glisic at coauthors [11]. The miscibility of triglycerides and methanol are rather poor due to molecular dissimilarity in size and polarity and therefore when in contact they form two liquid phases. The initial concentration of oil in the methanol at 20 °C is only about 3.7 g/L which could be almost neglected in terms of mole fraction [27]. Immiscibility of methanol and oil as well as reversibility of reaction requires that a large excess of methanol must be used (usually as molar ratio methanol to oil of 40:1 and more) for reaction realized without presence of a catalyst. Such initial ratio of oil and methanol will give a high yield of desired product (esters) mainly at supercritical condition, although desired and acceptable rate of reaction is also reported for synthesis at subcritical condition for methanol. A huge excess of methanol at specific condition of pressure and temperature is necessary for obtaining better miscibility between the methanol and the vegetable oil [10,11].

At atmospheric pressure methanol and triglycerides are almost immiscible up to 60 °C. Methanol become more soluble in vegetable oil with increase of pressure and temperature while, at the same time almost pure methanol (>99.7 mass%) represent the second liquid phase. In subcritical state of methanol (<240 °C and <8.0 MPa) the reaction mixture exists as two separate liquid phases. One is oil-rich phase and the other methanol-rich phase. An increase of temperature (and under the pressure which is slightly above the vapour pressure of methanol) the solubility of methanol in oil phase increases while only very small amount of oil dissolves in methanol-rich phase. The phase behavior of the binary vegetable oil and methanol or ethanol mixture can be categorized as Type II system [28]. This type of phase behavior is represented by the liquid–liquid equilibrium and it has been confirmed experimentally and by Vapour – Liquid Equilibrium (VLE) simulations [10–12,28,29]. The same phase behavior was confirmed for mixtures of ethanol and triglycerides [12].

A huge excess of methanol is necessary at high pressure and temperature in order to reach the complete miscibility of methanol and vegetable oil [11,12]. The creation of diglycerides and monoglycerides during alcoholysis of triglycerides, together with FAME/FAEE and glycerol which are the final products of reaction make this system very complex for analysis of phase equilibrium. As transesterification reaction proceeds at desired temperature and pressure, the composition and distribution of liquid phases is changing along with the content of compounds present in a reaction mixture, according to their solubility and affinity to methanol, oil or methyl esters [11,12]. The phase transition strongly depends on the temperature and pressure and the analysis of the experimental and simulated data of phase transition during reaction shows that four different and characteristic scenarios are possible. Moreover, along with changing composition and distribution of initially formed phases, the number of existing phases might change as well (depending on the pressure and temperature of reaction). The schematic diagram of phase transition at different conditions is shown in Fig. 1. Completely different compositions of phases (liquid 1, liquid 2 and liquid 3) from the first to fourth type (scenario) of phase transition has been observed, depending on the temperature and pressure [11,12]. Also, it should be noted that in all the cases, the vapour phase (pure methanol) exist in equilibrium with all identified liquid phases, but its molar quantity could be neglected.

The *first type* of phase transition is characteristic for temperature up to 170 °C and pressure below 1.5 MPa which might be characterized as high temperature and relatively low pressure for methanol. At the beginning of synthesis the reaction mixture (40:1 M ratio of alcohol to oil) is in equilibrium composed of two liquid phases; the alcohol-rich phase and the oil-rich phase (Fig. 1). The liquid 1 phase is almost pure methanol or ethanol (>99 mass%), while methanol or ethanol is present only in small quantity in liquid 2 phase (oil rich phase); the weight ratio of methanol to oil phase is 1:2 and corresponding molar ratio is 13:1 (Fig. 2). After first significant amount of glycerol is formed as well as a larger amount of FAME, the new liquid phase is created. The formation of this liquid phase could be explained by different (and better) solubility of glycerol in methanol than in methyl esters. After almost complete triglyceride′s conversion the weight ratio between phases in the reactor is practically constant: approximately 11:12:1 for Liquid 1: Liquid 2: Liquid 3, as well as the composition of these phases (Fig. 2 in [11]).

Finally at the end of reaction and complete conversion of triglycerides the oil rich phase disappear when only around 15 mass% of methanol is dissolved in FAME or biodiesel phase [11,12]. Up to 170 °C and 1.5 MPa the oil is present only in one liquid phase together with a smaller amount of dissolved methanol (methanol

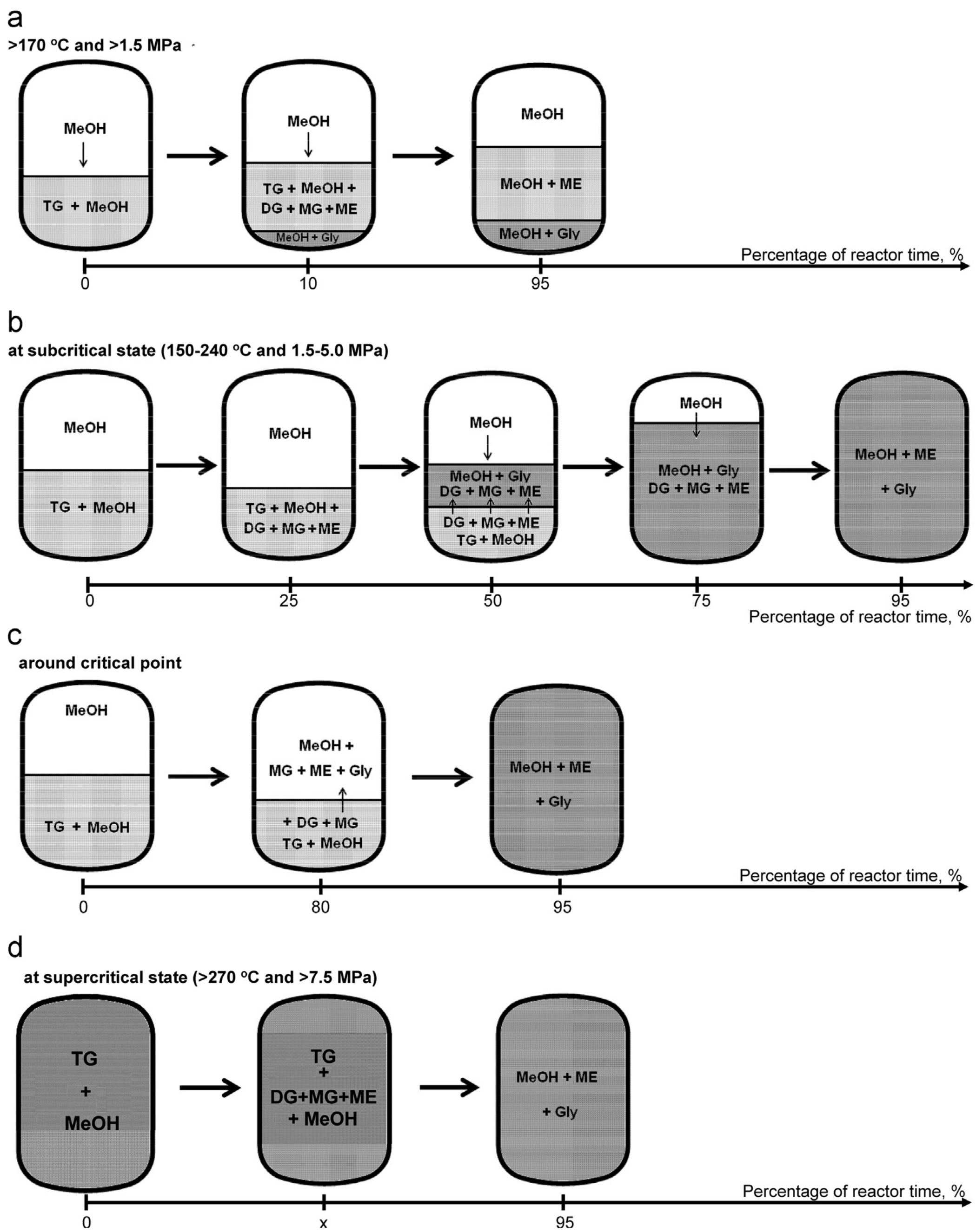


Fig. 1. The schematic diagram of the possible number of phases and phase compositions at elevated temperature and pressure during reaction.

to oil molar ratio is 1:1 which is three time less than stoichiometric ratio) which explains very slow reaction rate resulting in approximately 50 h required for complete conversion (without mixing).

The *second type* of phase transition exists at temperature and pressure below the critical point of methanol (temperature between 150 and 210 °C and pressure 1.5–5.0 MPa), corresponding to subcritical state of methanol. At the beginning of reaction at these conditions, the system of methanol and triglycerides is in liquid–liquid equilibrium with mass ratio of 46:54 (liquid 1–liquid 2 phase, 84:1 M ratio) where methanol is distributed between two liquid phases (25% of initial mass is dissolved in triglycerides i.e. in second liquid phase) [11,12] (Figs. 1 and 2). During the reaction, the amount of liquid 1 phase decreases while the liquid 2 phase increases. After one third of time required for complete reaction the third liquid phase is formed, following the liquid 1 phase disappearance, and close to the end of reaction, only one liquid phase exists.

Existence of several phases during reaction of triglycerides alcoholysis is stipulated by solubility of components, reactants and intermediary and final products as well. The liquid 1 phase contains mainly methanol (more than 99.8 mass% of methanol and up to 0.2 mass% of FAME) and could be designated as pure liquid methanol phase. The second liquid phase is mainly consisted of triglycerides with corresponding amount of solubilised methanol together with certain amount of intermediate products formed during reaction (diglycerides and monoglycerides; Fig. 2), as well as FAME. The third liquid phase is formed in the moment when the initial significant amount of glycerol is formed. Presence of glycerol changes the equilibrium composition and initiates the formation of separate third liquid phase. This phase is consisted

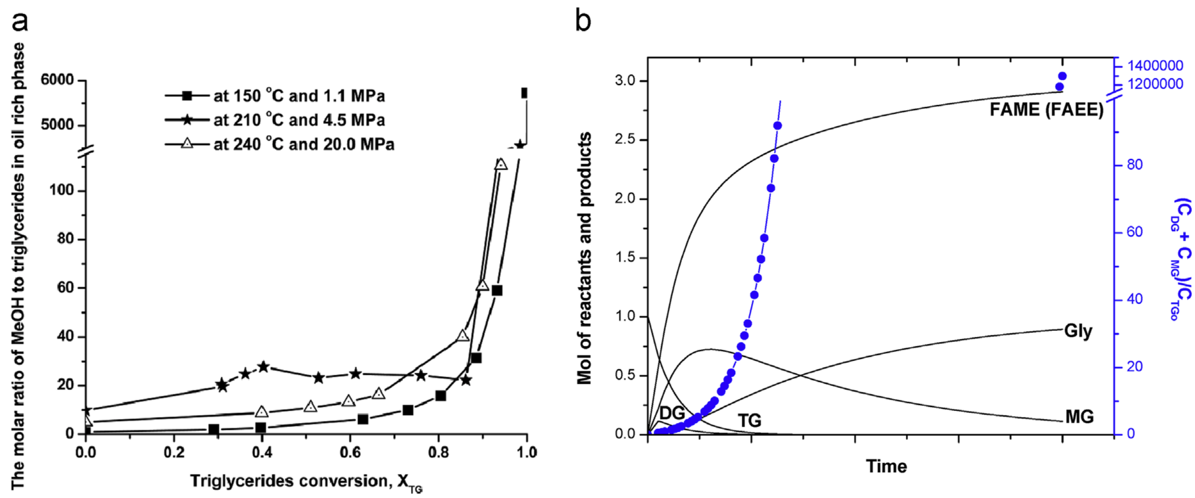


Fig. 2. The molar ratio of alcohol (methanol or ethanol) to triglycerides during reaction at different conditions (a) and molar ratio of sum of monoglycerides (MG) and diglycerides (DG) to triglycerides (TG) as parameter for mass transfer effects (b).

mainly of FAME, methanol and glycerol (with very small amount of monoglycerides) and could be designated as methyl esters phase. The molar ratio of methanol to FAME in the second liquid phase is 14:1 (mass ratio = 1:1.3) (Fig. 2). The mass ratio of two liquid phases (1 and 2) is 1.78 with distribution coefficient of methyl esters between the two phases of 2.1. The methanol to oil molar ratio in the oil phase changes during reaction from 6:1 to 10:1, consequently the resulting molar ratios of methanol to monoglycerides (MG) and to diglycerides (DG) in the oil phase are around 45:1 and even higher, for most of the reaction duration [11,12]. Such increase of molar ratio results in a higher reaction rate of reaction comparing to the rate for the first type of phase transition and approximately 10 h of is necessary for complete conversion of triglycerides. Methyl esters that are being formed by the reaction initiate the occurrence of new liquid phase which also contains: low concentrations of mono and diglycerides and glycerol, all of them dissolved in methanol [12]. Composition of the new liquid phase, in which concentration of glycerol together with corresponding concentration of FAME is increased, consequently increases the rate of reversible reaction. Namely, the reaction between glycerol and FAME is more probable than reaction between methanol and glycerides (DG and MG). At higher conversions of triglycerides (at 210 °C and 4.5 MPa), the only remaining liquid phase contains methanol, FAME, glycerol, as well as relatively small amount of monoglycerides and diglycerides [12]. These conditions lead to the increasing rate of reversible reaction, thereby reducing the level of equilibrium conversion and maximum attainable FAME yield. At the end of reaction one liquid phase contains methanol, FAME, glycerol, as well some small amount of monoglycerides and diglycerides (Fig. 1).

The *third type* of phase transition can be observed at temperatures near critical temperature (240–270 °C) and pressure above the critical pressure of methanol (20.0–28.0 MPa). At analyzed conditions, the system of methanol and triolein (initial molar ratio 42:1) was found to be at equilibrium of dense gas or supercritical phase and liquid phase. Performed calculation indicated that only at 270 °C and 20.0 MPa the whole system, from the beginning to the end of reaction contains single supercritical or dense gas phase. At the beginning of reaction the dense gas phase represents 44–56 mass% of whole reaction mixture depending on the temperature and pressure (Fig. 1). The composition of dense gas or supercritical phase is characterized by very high methanol content at the beginning of reaction, while with the increase of methyl esters yield the amount of esters (ME), monoglycerides (MG) and glycerol (Gly) also increase (ME up to 40 mass%; MG up to 10 mass %, Gly up to 5 mass%; Fig. 1). Such composition profile is related to the solubility of these components in the methanol at the observed temperature and pressure. Namely, the solubility of glycerides decreases in the series: Monoglycerides > Diglycerides > Triglycerides. In the oil phase (liquid phase, Fig. 1) at the beginning of reaction 30 mass% of methanol is soluble at 270 °C and 28.0 MPa and only 24 mass% at 240 °C and 20.0 MPa or 28.0 MPa. During the reaction, the mass of liquid (oil) phase decreases and disappears in the moment when almost complete conversion of triglycerides and corresponding yield of FAME is obtained. When conversion of triglycerides exceeds 95% the system containing FAME, glycerol and excess of methanol is present only in one dense (supercritical) gas phase and the composition of the only existing liquid phase is: 52.3 mass% of methanol, 42.4 mass% of fatty acid methyl ester and 5.3 mass% of glycerol [11,12].

When the pressure and temperature are above the critical one for the methanol the rate of reaction is increased mainly by the influence of temperature. Although solubility of methanol in oil phase at these conditions remains almost unchanged and very similar like solubility at 210 °C and 4.5 MPa (12:1 and more molar ratio of methanol and oil) it is important to underline that all products are completely soluble in the methanol phase [11,12]. Vegetable oil and methanol occur in two liquid phases at temperature up to 270 °C and pressures slightly below the vapour pressure of methanol at that temperature. Only at 270 °C and pressure which is much higher than the vapour pressure of methanol at this temperature (20.0 MPa) the single phase (supercritical or dense gas) is formed when molar ratio of methanol to oil at the beginning of reaction is 42:1. This is the *fourth type* of phase transition during reaction. The whole system is in supercritical or dense gas phase from the beginning to the end of methanolysis of triglycerides.

During methanolysis of triglycerides at different temperature and pressure the composition and distribution of liquid phases changes with the concentrations of compounds present in reaction mixture and their solubility and affinity to methanol and oil, or methyl esters. There is a change of composition and distribution of initially formed phases, but depending on temperature and pressure, the number of phases was changed accordingly. The rate of triglycerides methanolysis strongly depends on the oil and methanol concentration in oil rich phase.

Phase equilibrium is very important for understanding of the reaction mechanism and for the quantification of the rate of

triglycerides methanolysis. Furthermore, the knowledge of distribution of components between the phases in multiphase region is of interest for process design. Together with equilibrium and phase distribution data, it is very important to evaluate physical and thermodynamic properties of all reactant and products in biodiesel reaction, as well as the appropriate equation of state (RK-Aspen EOS) [11,30] which could describe well this complicated system.

2.1.1. Physical and thermodynamic properties and EOS for the reacting system

For the purpose of process design reliable and accurate physical and thermodynamic properties of pure components (measured data or predicted data using different methods) can play an important role in the final result. For vegetable oils or waste oils these properties canot be found in the literature, so for the estimation of physical and thermodynamic properties of pure compounds, the group contribution method can be applied as the most accurate one [10–12,30–42]. The method can be applied to the estimation of the following physical and thermodynamic properties of pure compounds: the normal boiling point, the critical pressure, the critical temperature, the critical volume, the standard enthalpy of vaporization at 298 K, the standard Gibbs energy, the standard enthalpy of formation at 298 K, the acentric factor and liquid molar volume at 298 K [20]. This method is very important for calculating the normal boiling point which is essential for separation processes and for the estimation of the critical properties.

The critical parameters for diolein, monoolein and methyl oleate were used for calculation of the phase equilibrium of complex mixture (alcohol–glycerides) at supercritical conditions [30], as shown in Table 1.

Estimation of critical parameters [30] was compared to available data in several other data bases. The critical temperature and critical pressure calculated by group contribution method were found to be different from corresponding values reported in ASPEN and especially in DIPPR data bases. The values of normal boiling point of analyzed glycerides and esters are very important for adequate and correct separation process (especially for distillation) which is one step in biodiesel synthesis, i.e. for recovery of excess of methanol and for purification of final products [9,30].

Large differences between calculated values of critical parameters and acentric factor and those presented in both data bases obviously exist [30]. The corrected data together with RK-Aspen EOS, were used for prediction of the phase equilibrium of complex reaction mixture at elevated pressure and temperature [30].

2.2. Reaction kinetics and process modeling

Non-catalytic biodiesel synthesis under elevated pressure and temperature is highly efficient in terms of triglycerides conversion, required reaction time and process layout. However, phase equilibrium and mass transfer can play an important role in the product distribution as well as the presence of reaction intermediates in the FAME final properties [11].

Investigation of subcritical and supercritical transesterification of triglycerides and the determination of kinetic parameters has been the objective of several articles published in the last several years [43–52] (Table 2). As can be observed, the most relevant papers related to kinetic investigation of supercritical transesterification assumed a simple first order irreversible reaction as an appropriate and acceptable kinetic model [46–52].

Unfortunately, such simple model did not explain the experimental data thoroughly at different pressures and temperatures. For the reaction at subcritical or supercritical conditions of an alcohol, the three step kinetic models (reversible or irreversible) were also tested [43,45–47] (Table 3).

Synthesis of biodiesel (triglycerides transesterification) is complex reaction which can be represented as the combination of three parallel and consecutive reversible reactions of the second order as mentioned previously [13,43]. The overall reaction occurs as a sequence of three steps, parallel with respect to alcohol and consecutive with respect to triglyceride. Triglyceride (TG) reacts with an alcohol (ROH) in the first reaction and forms diglyceride (DG) and fatty acid methyl ester (FAME). Monoglycerides (MG) and fatty acid methyl esters (FAME) are formed in the second reaction from diglyceride (DG) and methanol. The final products, appearing as products of the third reaction, are glycerol (GL) and again fatty acid methyl esters (FAME). The reaction scheme is shown below

$$TG + ROH \underset{k_{12}}{\overset{k_{11}}{\rightleftarrows}} DG + FAME \quad (1)$$

$$DG + ROH \underset{k_{22}}{\overset{k_{21}}{\rightleftarrows}} MG + FAME \quad (2)$$

$$MG + ROH \underset{k_{32}}{\overset{k_{31}}{\rightleftarrows}} GL + FAME \quad (3)$$

It is important to point out that the reversible reactions of DG, MG and GL with FAME control the maximum/equilibrium conversion of triglycerides. The composition of reaction mixture at the end of synthesis comprises mainly the following products: methyl esters (biodiesel), relatively small amount of glycerol and the large excess of alcohol. Monoglycerides and diglycerides are formed as intermediate products and could be present only in traces in a mixture upon reaction completion. However, those minute concentrations

Table 1
The physical and thermodynamic parameters of tri-, di-, mono-olein, methyl oleate, and ethyl oleate [30].

Parameter	Triolein	Diolein	Monoolein	Methyl oleate	Ethyl oleate
M (g/mol)	885.45	621.00	356.55	296.49	310.51
T_B (K)	827.40	765.03	674.82	595.93	617.00
V_B (m^3/kmol)	2.708	1.106	0.533	0.489	0.489
V_l (298 K), (m^3/kmol)	0.958	0.623	0.360	0.341	0.341
T_C (K)	977.88	920.20	835.06	721.02	764.00
P_C (bar)	3.34	5.05	10.56	11.03	12.80
V_C (m^3/kmol)	3.250	2.830	1.254	1.108	1.060
ω	1.9782	1.7632	1.5324	1.0494	1.0494
ΔG_f (298 K), (kJ/kmol)	−1.8E+05	−3.00E+05	−3.23E+05	−1.20E+05	−1.17E+06
ΔH_f (298 K), (kJ/kmol)	1.97E+05	8.08E+05	5.69E+05	−6.40E+05	−6.26E+05
ΔH_v (298 K), (kJ/kmol)	3.02E+05	2.19E+05	9.01E+04	6.36E+04	6.36E+04

M, g/mol – molecular weight; T_B, K – normal boiling point; V_B, m^3/kmol – liquid molar volume at T_B; V_l (298 K), m^3/kmol – liquid molar volume at 298 K; T_C, K – critical temperature; P_C, bar – critical pressure; V_C, m^3/kmol – liquid molar volume at critical point; ω–- acentric factor; ΔG_f (298 K), kJ/kmol – standard Gibbs energy at 298 K; ΔH_f (298 K), kJ/kmol – standard enthalpy of formation at 298 K; and ΔH_v (298 K), kJ/kmol – standard enthalpy of vaporization at 298 K.

Table 2
The literature review of kinetic model at sub and supercritical conditions.

Reference	**Oil. Oil: alcohol** mol ratio	***T*** (°C)	***P***, (Pa)	**Constant** (s^{-1})	$\mathbf{E_a}$ (kJ/mol)	***A*** ($kg_{mixture}$/ $kg_{alcohol}$/s)	**Kinetic model**
Kusdiana and Saka [46]	Rapeseed oil 1:42	270 –487	12.0–105.0	at 270 °C $k_1=7.0\times10^{-4}$ at 487 °C $k_1=8.0\times10^{-2}$	$E_{a1}=59.1$ $E_{a2}=52.7$ $E_{a3}=45.7$	8.32×10^4	One summarized first order irreversible
Madras et al. [48]	Sunflower oil 1:40 Methanol and ethanol	200 –400	20.0	1.67×10^{-6} – 5.5×10^{-4} 5.3×10^{-4}– 1.07×10^{-3}	3 for methanol 2 for ethanol	3.65×10^{-6} 8.81×10^{-4}	One summarized first order irreversible
Song et al. [49]	Palm oil	200 –400	< 40.0	1.03×10^{-6}– 2.93×10^{-3}	105.27	4.34×10^5	"Second order" $dC_{TG}/dt=-kC_{TG}^{0.9565}C_{MeOH}^{1.0493}$
Varma and Madras [50]	Canola and Linseed oil 1:40	200–350	20.0	$k_1=6.9\times10^{-4}$ at 300 °C	70	1.66×10^4	One summarized first order irreversible
Silva et al. [51]	Soybean oil :40 ethanol	275 300 320 350	20.0	$k_1=2.12\times10^{-4}$ $k_1=3.12\times10^{-4}$ $k_1=8.18\times10^{-4}$ $k_1=1.67\times10^{-3}$	78.7	6.73×10^4	One summarized first order irreversible
He and Sun [52]	Soybean Oil, 1:40 methanol	210 –280	28.0	1.19–8.81 $\times10^{-4}$	11.2 Subcritical 56.0 supercritical	-	One summarized first order irreversible

Table 3
The literature review and comparison with the data obtained in this study.

References	***T*** (°C)	$kg_{mixture}/mol_{methanol}$/s			$\mathbf{E_a}$ (kJ/mol)	***A*** ($kg_{mixture}$/ $mol_{methanol}$/s)	**Proposed model**
		$\mathbf{k_1}$ **and** $\mathbf{k_{11}}$	$\mathbf{k_2}$ **and** $\mathbf{k_{22}}$	$\mathbf{k_3}$ **and** $\mathbf{k_{33}}$			
Diasakou et al. [45]	220 (55 bar) 235 (60 bar)	$k_1=8.17\times10^{-6}$ $k_1=1.90\times10^{-5}$	$k_2=6.67\times10^{-6}$ $k_2=1.67\times10^{-6}$	$k_3=3.0\times10^{-6}$ $k_3=2.4\times10^{-6}$	$E_{a1}=117$ $E_{a2}=128$	–	Second order irreversible reaction
Wenzel et al. [47]	220 (55 bar) 235 (60 bar)	 $k_1=9.17\times10^{-6}$ $k_{11}=5.28\times10^{-6}$ $k_1=2.07\times10^{-5}$ $k_{11}=1.25\times10^{-6}$	 $k_2=7.78\times10^{-6}$ $k_{22}=5.0\times10^{-6}$ $k_2=1.87\times10^{-5}$ $k_{22}=9.31\times10^{-6}$	 $k_3=2.78\times10^{-6}$ $k_{33}=2.5\times10^{-6}$ $k_3=3.03\times10^{-6}$ $k_{33}=5.56\times10^{-8}$	$E_{a1}=113$ $E_{a11}=-200$ $E_{a2}=122$ $E_{a22}=86.3$ $E_{a3}=119.7$ $E_{a33}=-529$	3.15×10^{10} 1.22×10^{-21} 2.35×10^{11} 2.47×10^7 1.85×10^{-1} 8.89×10^{-59}	Second order reversible reaction
		$\mathbf{m^3/s/kmol}$					
Glisic and Orlovic [43]	150 (11 bar) 210 (45 bar)	$k_1=5.49\times10^{-6}$ $k_{11}=2.30\times10^{-6}$ $k_1=1.87\times10^{-4}$ $k_{11}=1.11\times10^{-4}$	$k_2=4.59\times10^{-6}$ $k_{22}=6.09\times10^{-7}$ $k_2=6.85\times10^{-5}$ $k_{22}=1.28\times10^{-5}$	$k_3=1.28\times10^{-6}$ $k_{33}=1.98\times10^{-7}$ $k_3=5.71\times10^{-5}$ $k_{33}=1.34\times10^{-5}$	$E_{a1}=72.8$ $E_{a2}=83.5$ $E_{a3}=68.0$	–	Second order reversible reaction
References	***T*** (°C)	1/s			$\mathbf{E_a}$ (kJ/mol)	***A*** (1/s)	**Proposed model**
		$\mathbf{k_1}$	$\mathbf{k_2}$	$\mathbf{k_3}$			
Kusdiana and Saka [46]	210 (100 bar)	$k_1=3.0\times10^{-5}$	$k_2=1.0\times10^{-5}$	$k_3=8.7\times10^{-4}$	$E_{a1}=59.1$ $E_{a2}=52.7$ $E_{a3}=45.7$	–	First order irreversible reaction

of reaction intermediates could impact the biodiesel quality and compliance with the current technical standards. It is therefore important to be able to predict an optimum reaction time, or a reactor space time. This reaction was investigated under subcritical or supercritical conditions of methanol and it has been shown that reaction mixture undergoes complex phase transition accompanied by a resulting mass transfer phenomena [11,12].

Triglycerides transesterification under elevated pressure and temperature is highly sensitive to different variables influencing the rate of reaction, and among them the molar ratio of alcohol to oil seems to be the most important. Additional factors influencing the process are related to phase equilibrium at operating conditions: reaction in single supercritical phase, reaction in two separate liquid phases or reaction in a multi-phase system. These different reaction environments depend on the temperature, pressure, alcohol to oil molar ratio and the actual reaction mixture composition [11,12]. Although the transesterification of triglycerides at higher temperature and pressure has been analyzed in great detail, the kinetic expression which could correlate the experimental data over wider range of pressure and temperature have focused on finding the best fit of simple kinetic models (first order kinetics or single overall reaction) to experimental data [43–52]. More detailed kinetic model of non-catalytic triglycerides transesterification at elevated temperatures and pressures was developed using simplified procedure to calculate kinetic parameters [43]. The phase distribution of reacting species and mass transfer of reacting species were considered in model development. All consecutive reaction steps in this complex reaction were treated as reversible reactions and the model was found to fit very well the experimental data regarding concentrations of methyl

esters, methanol, glycerol and triglycerides. However the prediction of concentrations of intermediates, mono- and diglycerides, was relatively poor. The ability to predict concentrations of intermediates with good accuracy is vital since these compounds, as noted previously, could have negative impact on the biodiesel quality.

2.2.1. Kinetic models

The reaction rate for each component in the system (r_i where i=*TG, DG, MG, FAME, ROH, GL*) (constant volume batch system, time, *t*, dependent) can be represented by the following set of equations where each reaction step is assumed to be second order in both directions and therefore dependent on concentration of reacting components (C_i where i=*TG, DG, MG, FAME, ROH, GL*) (Eqs. 4–9) [43,44]:

$$r_{TG}=\frac{dC_{TG}}{dt}=-k_{11}C_{TG}C_{ROH}+k_{12}C_{DG}C_{FAME} \tag{4}$$

$$r_{DG}=\frac{dC_{DG}}{dt}=k_{11}C_{TG}C_{ROH}-k_{12}C_{DG}C_{FAME}-k_{21}C_{DG}C_{ROH}+k_{22}C_{MG}C_{FAME} \tag{5}$$

$$r_{MG}=\frac{dC_{MG}}{dt}=k_{21}C_{DG}C_{ROH}-k_{22}C_{MG}C_{FAME}-k_{31}C_{MG}C_{ROH}+k_{32}C_{GL}C_{FAME} \tag{6}$$

$$r_{GL}=\frac{dC_{GL}}{dt}=k_{31}C_{MG}C_{ROH}-k_{32}C_{GL}C_{FAME} \tag{7}$$

$$r_{FAME}=\frac{dC_{FAME}}{dt}=-3\left(\frac{dC_{TG}}{dt}\right)-2\left(\frac{dC_{DG}}{dt}\right)-\left(\frac{dC_{MG}}{dt}\right) \tag{8}$$

$$r_{ROH}=\frac{dC_{ROH}}{dt}=-\frac{dC_{FAME}}{dt} \tag{9}$$

If the reaction scheme is represented by the above equations the concentrations of reacting species are assumed to be numbers of moles divided by the overall reaction volume, regardless of the existence of multiple phases. Each reaction is characterized by its reaction rate constant (k_i where i=11, 21, 31 for forward reaction and 12, 22, 32 for reverse reaction, Eqs. 1–3). The slowest forward reaction rate controls the overall reaction rate along with reaction equilibrium constant for each of the reversible reactions shown above [43,44].

2.2.2. The influence of mass transfer limitations on the reaction kinetics – mass transfer limitation in continuous phase

The mass transfer of alcohol from the alcohol phase towards the alcohol–oil interface could be the critical step limiting the rate of transesterification reaction, since the reaction mixture is heterogeneous and consists of two immiscible liquid phases [11]. Poor mass transfer between two phases in the initial phase of the reaction results in low reaction rate. Besides this, the low solubility of alcohol in the oil phase can also limit the rate of transesterification reaction in its early stages [27]. During the initial period of reaction, the overall reaction rate is thus limited by the rate of mass transfer of TG from the bulk oil phase towards the interface with alcohol rich phase.

The sigmoid shape of the conversion curves during FAME synthesis points out to a changing reaction mechanism. Initially slow reaction rate increases with conversion and in its final stage, the rate curve reaches a plateau. At the beginning of reaction, the interfacial area is dependent on the agitation intensity and mass transfer controls the overall reaction rate ($k_{kinetic}$»$k_{mass\ transfer}$) [43,44]. The following increased reaction rate can be explained by the "self-enhancement" of the interfacial area, causing the increase of the rate of mass transfer. From the fact that the interfacial area increases one can conclude that the overall rate of reaction occurring at the interface will also be enhanced progressively. Additionally, the formation of intermediate products (mono and diglycerides) which are known as surface active compounds, as well as FAME formation, will inhibit the drop coalescence and favor formation of a stable emulsion of very small droplets. By the formation of surfactants, the interfacial area increases rapidly and the reaction shifts to the kinetically controlled regime, which is temperature dependent (Fig. 2b).

Consequently, the enhanced interfacial area of the reaction mixture provides possibility to consider the system as a pseudo-homogeneous one, in which the chemical reaction controls the overall kinetics [43,44]. Therefore, the kinetic constant for the forward reaction of triglycerides conversion could be corrected with following equation, introducing the mass transfer effects:

$$k_{11}{}'=k_{mt}+k_{11}(C_{DG}+C_{MG})/C_{TGo} \tag{10}$$

where k_{mt} represent the mass transfer controlled kinetic constant in the initial phase of the reaction and C_{TGo} is starting concentration of triglycerides.

Increasing conversion followed by changing phase distribution, increasing concentrations of intermediates (mono and diglycerides) and the enhancement of interfacial area, results in the increased overall kinetic constant. The second constituent in the above shown equation will increase with rising concentrations of DG and MG, as the consequence of enlarged molecular fluxes. The mass transfer controlled kinetic constant have a value for approximately one magnitude lower value then kinetic constant of forward reaction of first step.

2.2.3. Kinetic parameters for complex reaction scheme

The kinetic constants for forward and reverse reaction steps were obtained by Genetic Algorithm (GA) [44]. The complex kinetic model and kinetic parameters determined by the GA method, with the inclusion of mass transfer limitations, fitted well the experimental data (Fig. 3). The predictions of triglycerides conversion and FAME yield were very good as well as the predicted concentrations of intermediates (mono- and diglycerides).

Within the broad range of analyzed pressure and temperature conditions (150–400 °C and pressures from 4.5 MPa to 28.0 MPa) the proposed model is reasonably accurate and the accuracy is usually better than with other models. This is mainly the consequence of taking into consideration the phase equilibrium and the distribution of reacting species between phases in contact [43,44]. Also, the model considers the equilibrium conversion of glycerides (mainly MG) which depends on the existing number of phases during transesterification (most importantly at the end of reaction thereby limiting equilibrium conversion) (Fig. 3). The overall reaction rate is therefore determined by the reaction rate of last consecutive step which is also influenced by reversible reaction between FAME and glycerol. Very close to the end of reaction, the molar concentration of FAME and glycerol is much higher than corresponding molar concentration of glycerides (mainly monoglycerides and diglycerides) and methanol, which has additional negative influence on the overall reaction rate [43,44].

The kinetic constants are mainly dependent on the temperature but they are also function of methanol to glycerides molar ratio. When both temperature and pressure are within subcritical conditions of methanol (< 210 °C and < 4.5 MPa) the overall reaction rate can be limited by the mass transfer of reacting species, but only at the beginning of reaction. At subcritical conditions the two liquid phases exist in the initial phase and the molar ratio of methanol to oil, in the phase in which the reaction takes place, increases with increasing temperature (from 150 °C to 240 °C) from 1:1 to 20:1. At supercritical conditions the ratio will immediately reach value of 42:1 since only one phase exists, which remains as the only phase throughout the synthesis. Very good agreement of

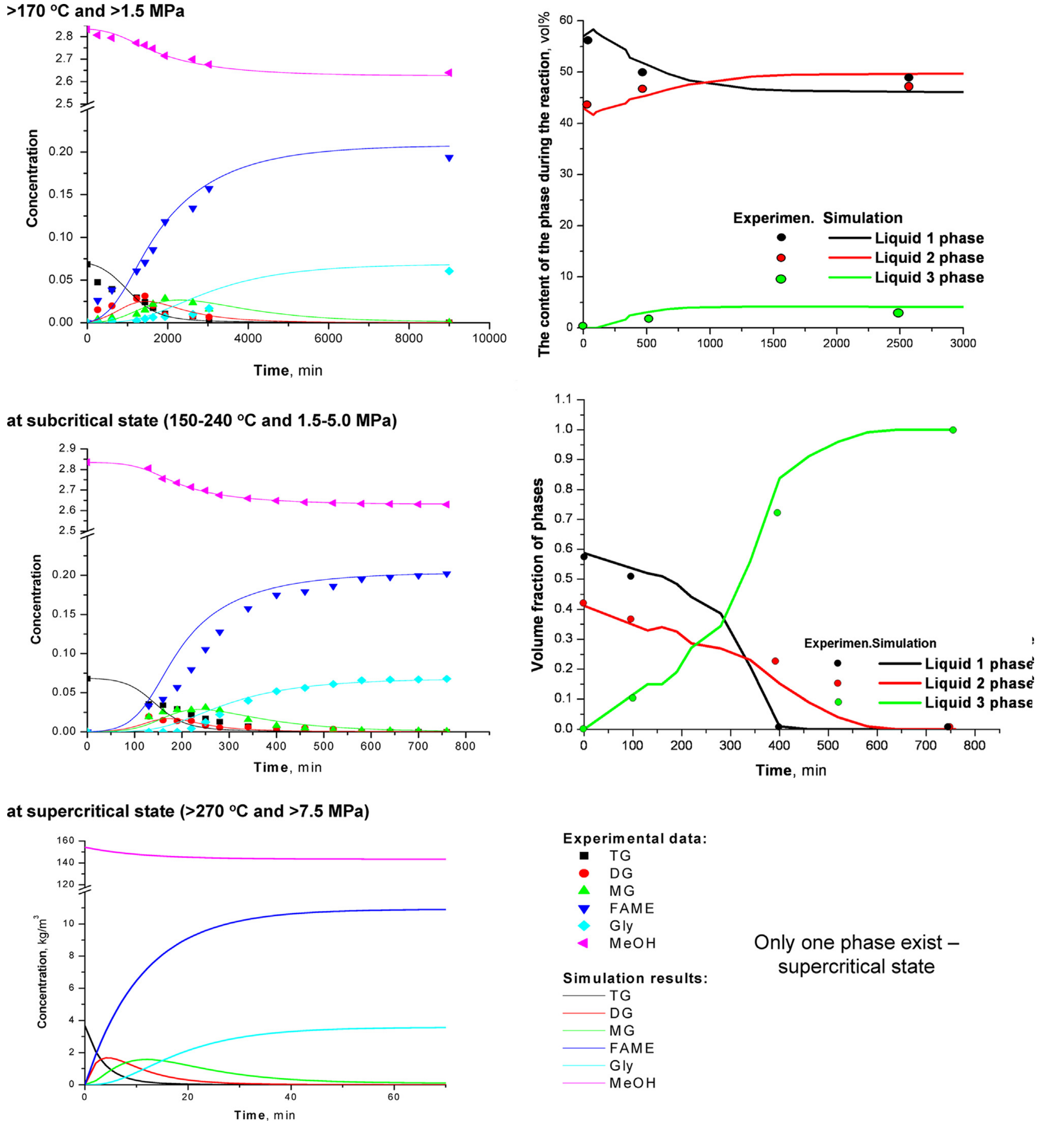


Fig. 3. The experimental data and simulation results obtained by proposed kinetic model and GA optimization technique at different T and p (left side) with the phases change in reactor during reaction time (right side).

simulation results and experimental data indicates also that the rate of triglycerides transesterification, or overall reaction rate, depends strongly on the oil to methanol ratio in the oil rich phase.

The obtained results indicate that the net reaction rates of monoglycerides (k_{MG}) and diglycerides (k_{DG}) disappearance are lower than the net reaction rate of triglycerides (k_{TG}) (descending order of reaction rate constants is: $k_{TG} > k_{DG} > k_{MG}$) [43,44]. This is in accordance with theory of the role of methoxy ion and structural orientation of molecules in defining the reaction rates between different glycerides and methanol [14,43]. The theory also concluded that there is no significant influence of: the number of double bonds, or *cis* and *trans* configurations, and the chain length of triglycerides, on the overall reaction rate which is very important for waste oil utilization. The only parameter which influenced the values of reaction rate constants was found to be the solubility of different triglycerides in methanol [14,43], as additionally confirmed by the analysis of activation energy values. This is further confirmed by the residual small amounts of monoglycerides and diglycerides which remain in reaction mixture at the end of reaction.

Even if the triglycerides are most reactive, the apparent kinetic constants for reaction of triglycerides and methanol have lower value due to mass transfer limitations (at subcritical conditions characterized by simultaneous existence of two liquid phases). Using this correction it was found that the net rate of diglycerides

Table 4
Summary of kinetic constants value, phase equilibria and conversion data [43,44].

Parameters	Supercritical conditions				Around critical point			Subcritical conditions		
Temperature (°C)	400	350	300	280	270	260	250	240	210	150
Pressure (MPa)	20.0	20.0	20.0	28.0	28.0	28.0	28.0	28.0	4.5	1.1
Equilibrium conversion $(X)_e$	0.998	0.998	0.970	0.950	0.970	0.982	0.990	0.995	0.986	0.990
Time for equilibrium conversion, average (min)	From 3 to 30 min depending on published data (all in 1–3 ml volume reactor) [44,46,52]				60	65	70	–	800	9000
Number of phases	One				2 At the beginning 1 at the end			Two	2 or 3 At the beginning, 1 at the end	2 or 3 At the beginning, 2 at the end
Magnitude of kinetic constant:										
Forward reactions	10^0	10^0	10^{-1}	10^{-1}	10^{-2}	10^{-3}	10^{-3}	10^{-3}	10^{-4}–10^{-5}	10^{-5}–10^{-6}
Reverse reactions	10^{-2}	10^{-2}	10^{-2}	10^{-2}	10^{-3}	10^{-4}	10^{-4}	10^{-4}	10^{-4}–10^{-6}	10^{-6}–10^{-9}

disappearance has the highest value and that the order of reaction rate constants is: $k_{DG} > k_{MG} > k_{TG}$. It can be observed that the reaction rate constants are not only a function of temperature, but they also depend on the pressure. This observation can be explained by the increase of methanol solubility in oil at higher pressure and temperature and thus the increase of methanol to oil molar ratio [43,44].

This conclusion is the consequence of the fact that glycerol and FAME remain in different liquid phases during reaction which makes the reversible reaction less possible (equilibrium conversion is close to 1). At supercritical conditions of alcohol, it can be seen that equilibrium conversions decrease with temperature increase while at 300 °C and higher they increase again to a value close to 1 (Table 4). Such behavior could be explained by the glycerol decomposition at high temperatures and thus decreased influence of reversible reaction between FAME and glycerol. Glycerol polymerization and polyglycerols formation is another possible reaction at high temperature. Such condensation reactions are known to occur at high temperatures forming hydroxylated chains capable of reacting further [34,54–64]. Above the temperature of 300 °C, esters, glycerol and glycerides decomposition starts after 60 min before reaching conversion of 96%, depending of molar ratio of alcohol to oil, pressure conditions and time of reaction. At higher temperature the decomposition of esters, glycerol and glycerides occurs progressively.

Kinetic parameters for complex reaction scheme including all forward and reverse reaction of triglycerides alcoholysis under high pressure and temperature [43,44] were found to be superior in predicting concentration profiles of diglycerides and monoglycerides. The ability to predict accurately concentrations of intermediates could be of crucial importance for proper design of reactor system for FAME synthesis (Fig. 4). This is in fact critical parameter for FAME biodiesel quality due to limitations imposed by pertaining technical standards. Moreover, the calculations of activation energies of forward reactions are in very good agreement with values obtained by molecular orbital calculations [44,65–67] (Table 3).

The summary of kinetic constants value, phase equilibria and conversion data is shown in Table 4.

2.3. Process design

In order to produce biodiesel which meets requirements set by EN 14214:2012 or ASTM 6751-12 it is necessary to follow a strict procedure for input materials (including waste edible oils), operating reaction and separation conditions, use of different types of catalysts (homogeneous or heterogeneous), process layout, specific energy consumption etc. Among several phases in FAME or FAEE synthesis the reaction procedure is most important since it determines product quality as well as type and severity of purification section (esters and glycerol purification). The advantages of supercritical alcoholysis of triglycerides (SCA) could be summarized as follows: a high reaction rates can reduce the reactor volume, while the absence of the catalyst simplifies the purification procedures (this is especially the case for conventional technology which uses homogeneous catalyst dissolved in the reaction mixture, and also homogeneous catalyst with excessive leaching of active species during reaction). Another important advantage of SCA process is that if feedstock free fatty acids content is high (FFA are known to be present in higher concentrations in waste oils) there will no consequences on the process and product quality since free fatty acids will be easily converted to FAME. This is not the case for conventional homogeneously catalyzed process and for process catalyzed by heterogeneous catalyst which undergoes leaching during reaction. However, the main disadvantage of SCA is always related to the questions: “What is the total energy consumption of SCA process comparing to conventional synthesis (e.g. homogenous alkali catalyzed alcoholysis – HACA)?” and “Is it possible to reduce the energy consumption while retaining all obvious advantages of SCA process”?

Modeling of biodiesel synthesis under elevated pressure and temperature has been focused of several articles published in literature [6,9,68–98] over the past ten years. Authors of these papers have mainly used information and data related to kinetics and thermodynamics of reaction between methanol and triglycerides from the available literature sources, and made different assumptions which are necessary to perform the preliminary design of industrial plant. However, inadequate parameters and assumptions used in some calculations and process modeling could also lead to ambiguous conclusions and sometimes erroneous conclusions. The problem of insufficiency data for detailed process design was in the focus of paper published by Glisic and Skala [9]. Process flowsheet for continuous biodiesel production from triglycerides under supercritical conditions of alcohol (SCA) was analyzed and the influence of triglycerides conversion degree on the overall energy consumption of SCA was examined. A comparison between the homogenous alkali-catalyzed alcoholysis (HACA) and the supercritical methanolysis of triglyceride was made in order to point out the advantages and disadvantages of each of the analyzed processes. Furthermore, the energy consumption for each process step and environmentally weak points of both processes were discussed and possible solutions to tackle these problems were proposed.

The typical process flowsheet of SCA is presented in Fig. 5. Inlet stream, containing methanol and waste oil, is mixed with recycled methanol stream (molar ratio of 42:1) and heated up in the heat

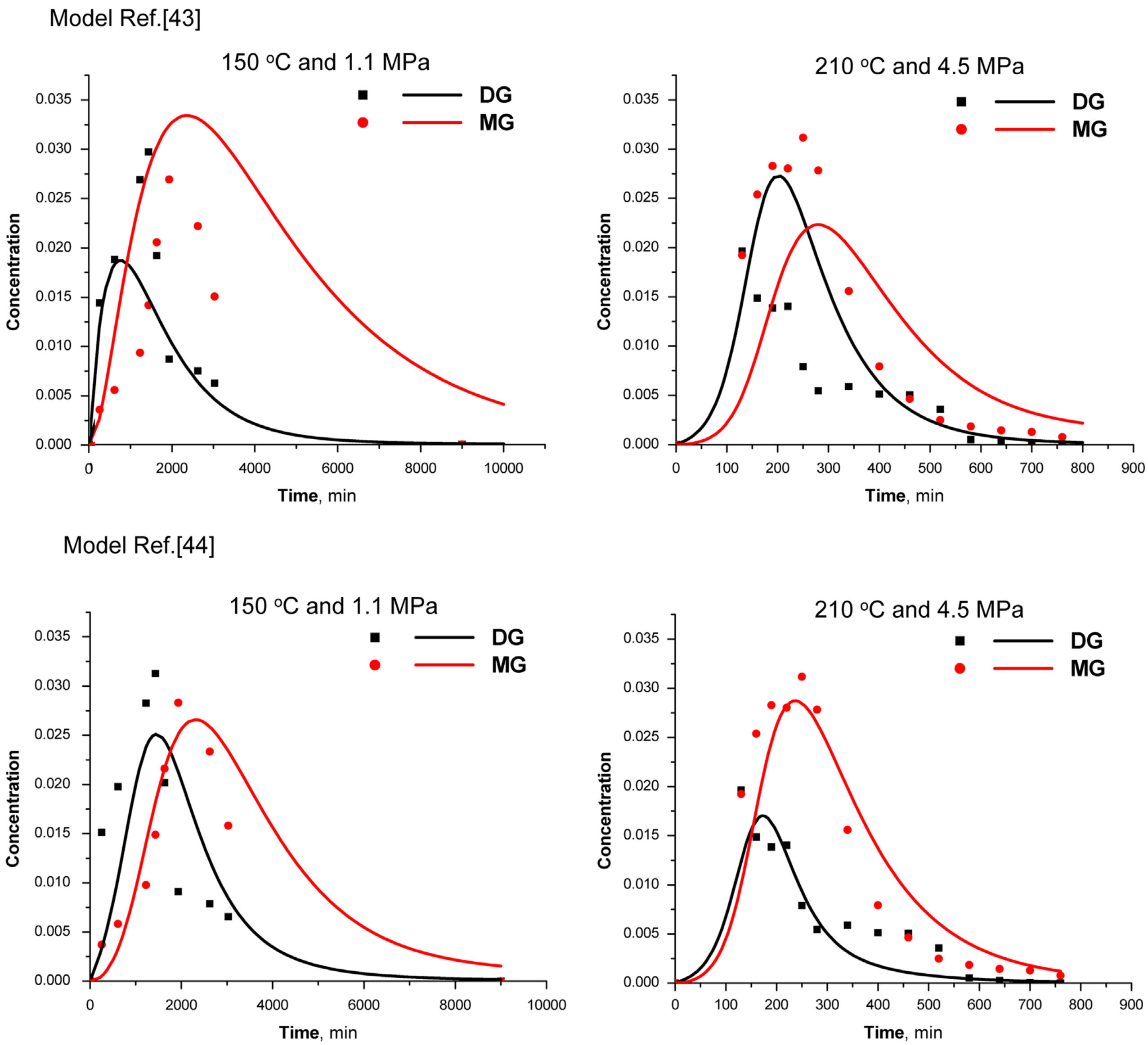


Fig. 4. Different model comparison in predicting concentration profiles of diglycerides and monoglycerides.

exchanger, followed by pressure increase prior to the plug flow reactor. Reactor outlet stream is cooled down and depressurized, with the typical biodiesel yield of 95–97 mass%. The excess methanol has to be recycled into the process and this is done in distillation column (four theoretical stages operating with reflux ratio 2, at 0.003 MPa and 100 °C) where methanol is the overhead product with almost 100% purity. Bottom product from distillation column consists mainly of esters, glycerol, triglycerides and methanol, and this stream is further treated in gravity separator. Upon separation, upper layer (esters >95.3 mass%, methanol containing low concentration of glycerol and triglycerides) is separated in vacuum distillation column (five theoretical stages and operating with reflux ratio 2, at 0.002 MPa and 298.8 °C in reboiler) in order to prevent degradation of esters and glycerol. The resulting distillate stream contains 99.8 mass% of esters. Further, the production of biodiesel could be much more economical if such process scheme provides possibility to produce glycerol of pharmaceutical grade (>99.5 mass%) in another vacuum distillation column with five theoretical stages and operating using the reflux ratio of 2.

SCA requires larger amount of energy for heating the feed but a high degree of conversions of triglycerides can be achieved without use of catalyst in less than 30 min of space time (Table 5). Although, the flow of feedstock into the chemical reactor operating at supercritical conditions is much higher due to the high molar ratio of methanol to oil, a total volume of reactor in the case of SCA is smaller than the volume necessary for realizing methanolysis catalyzed by alkali at lower temperature, as a consequence of high reaction rate. On the other hand, the SCA also contains a system used to exchange the heat between hot and cold streams thus optimizing the total energy consumption. Such solution has advantage because heating oil can also supply required amount of energy to the reboiler in distillation columns necessary for the final purification of FAME and glycerol. The ratio of methanol to oil plays an important role in SCA for achieving desired solubility of oil in methanol [41,42]. A high ratio of methanol to oil applied in SCA has disadvantage in posterior process stages. The excess of methanol must be recycled and separated from reaction mixture in a distillation column thus increasing total energy consumption. On the other side, the presence of a catalyst in the reaction mixture of HACA process makes the purification of the FAME more complex producing a larger amount of wastewater and other solid waste [47].

Namely, energy necessary for recycling a large excess of methanol is about 48% of total amount of consumed energy and

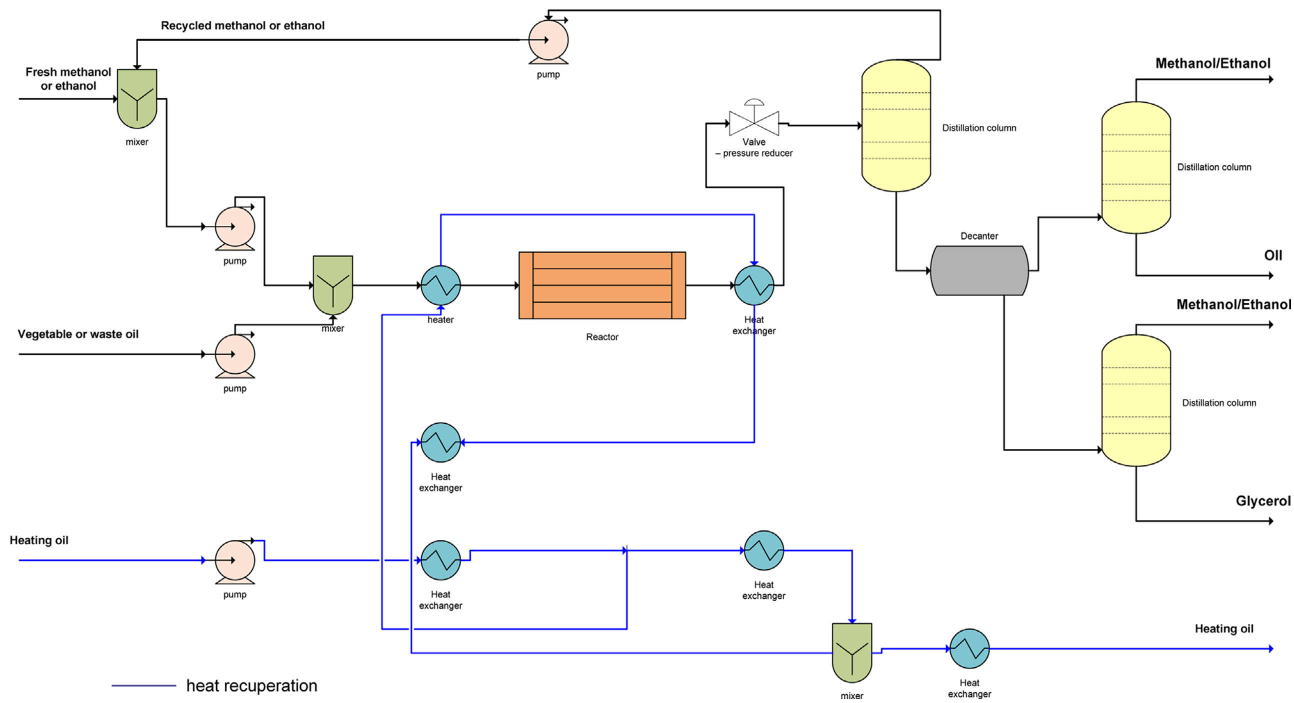


Fig. 5. The typical process flowsheet of sup or supercritical alcoholysis (SCA).

Table 5
Comparison of alkali-catalyzed (HACA) and supercritical process (SCA) operating conditions, triglycerides conversion and raw material flow for capacity of 10,000 t/year [9,10].

Process description	Supercritical process (SCA)	Alkali catalyzed process (HACA)
Material		
Alcohol (kg/h)	1948	247
Waste oil (kg/h)	1282	1307
Sodium hydroxide (kg/h)	–	10.1
Phosphoric acid (kg/h)	–	8.3
Water (kg/h)	–	200
Molar ratio (alcohol to oil)	42:1	6:1
Process conditions		
Reaction time	120–400 s	1.8 h
Temperature (°C)	280	60
Pressure (MPa)	20	0.4
Conversion (%)	97	95
Catalyst	–	NaOH
Process equipments		
Reactor	1	2
Reactor type	Plug flow	CSTR
Pumps	5	6
Distillation columns	3	3
Heat Exchangers	7	8
Gravity separator	1	1
Equipment	**Energy consumption** (kW)	
Preheater	1130	28
Recovery of methanol (reboiler)	1563	157
Purification of FAME (reboiler)	520	639
Purification of glycerol (reboiler)	18	463
Salt removing (evaporator)	–	1039
Heat recovery	824	–
Total	**2407**	**2326**

it could not be changed substantially by increasing or decreasing conversion of triglycerides. It is important to point out that the conversion of triglyceride does not have effects on energy consumed for purification of glycerol. Namely, the change of conversion of triglycerides from 85 to 100% required consumption of energy in reboiler of distillation column from 16 to 23 kW [6,9,68]. Energy for purification of methyl esters increases for 52% if conversion of triglycerides decreases from 97% to 85% but in total energy consumption it increases by only 4.2%. Furthermore, the lower conversion of triglycerides requires that distillation column used for purification of FAME has more stages. According to this calculation and obtained results it obviously seems that main course in further development of biodiesel synthesis under higher pressure is also related to substantial decrease of methanol to oil ratio as well as to decrease synthesis temperature. These requirements could be only satisfied if biodiesel synthesis is performed using heterogeneous catalyst.

Knowing all economical and environmental drawbacks of homogeneously catalyzed alkaline process (currently the main process applied in the industry) many investigations have started with a goal to develop new and more efficient and robust technology for FAME production, and these include the above mentioned SCA or synthesis under subcritical conditions of methanol with heterogeneous catalyst (H-SubCA). The overall energy consumption and thus the cost of biodiesel production could be reduced by application of such efficient processing technology. Related to the energy consumption, two comparatively analyzed technologies, the SCA and HACA, result in almost the same energy consumption [9]. However, the advantage of SCA obviously exists because it allows use of low price feedstock (vegetable oil containing larger amount of free fatty acids, FFA) [6,9,68]. The price of such feedstock has significant influence on total biodiesel manufacturing cost (60–80% of the total cost of biodiesel production cost). However the significant volume of consumed energy and thus the cost of biodiesel production is contributed by several steps of SCA (separation of large excess of methanol from reaction mixture, the reaction mixture heating

above 250 °C, pumping to high pressure of 10 MPa and higher). However, SCA technology is despite all these drawbacks prospective since it enables conversion of cheaper feeds into FAME, which is not the case for conventional HACA process.

HACA process is usually performed at lower temperature (about 80 °C) using moderate excess of methanol, and, followed by removal of catalysts after reaction which requires substantial amount of energy. Also, a large amount of wastewater is produced during separation and purification of the final products and catalyst neutralization [9]. Thus, the replacement of homogenous with heterogeneous catalyst has many advantages. The heterogeneous catalyst could be easily separated from the reaction mixture by filtration without requiring the use of a solvent, catalyst could be regenerated after use in one and reuse in the next batch, and has a less corrosive character than alkali or acid (traditional homogeneous catalyst for alcoholysis of triglycerides), leading to safer, cheaper and more environment-friendly operation.

2.4. Process improvement for energy efficiency

One can expect that the problem of high energy consumption for preheating of reaction mixture could be avoided if temperature and pressure of methanolysis is decreased from supercritical (280 °C and 28 MPa) to subcritical conditions (150 °C and 20 MPa) (Fig. 6a and b). However, at lower temperature and pressure the reaction rate is slow (Table 4) and thus without substantial change of residence time of reaction mixture in reactor only 80.9% conversions of triglycerides could be obtained. Lower conversion and specified FAME production capacity require a higher input of oil and methanol into a reactor. However, this variant of FAME industrial synthesis would require a higher investment (the higher equipment and plant cost) and requires also recycling of unused oil into the process. Furthermore, a lower conversion of triglycerides requires an additional purification of glycerol and methyl esters and thus more energy will be used (67% more for FAME purification and almost three times higher energy demand for glycerol purification) [68]. This means that almost the same amount energy is necessary for supercritical and subcritical FAME synthesis if heat recuperation is not used at supercritical conditions (Fig. 6a and b). Results of these simulations indicate that although subcritical methanolysis could be performed at lower temperature and pressure, the total energy consumption will be higher for almost 30% compared to the process of FAME synthesis conducted at supercritical conditions (2422–3135 kW) [68]. To solve the problem of lower conversion of triglycerides at subcritical conditions (Fig. 6a) the appropriate and efficient catalyst should be applied (using the same value of reaction rate constant as used for simulation of methanolysis at supercritical conditions) (Fig. 6c).

Comparing obtained results one can conclude that for the same degree of conversion of triglycerides and for a larger difference in temperature and pressure at which FAME is synthesized (280 °C and 28 MPa compared to 150 °C and 20 MPa), the total energy consumption is almost the same (the difference is almost negligible) (Fig. 6b and c). Namely, the energy which might be obtained from the reaction mixture leaving chemical reactor could be used in corresponding heat exchangers system if synthesis is performed at supercritical conditions. This means that synthesis under supercritical conditions i.e. at higher temperature and also under higher pressure does not necessarily increase total energy consumption for FAME production.

The energy necessary for methanol recovery is the largest part of energy consumption required in the process of FAME synthesis at supercritical conditions [9] and non-catalytic subcritical conditions. At the supercritical conditions it represents 46.5% of the total energy consumption and at subcritical conditions performed with appropriate heterogeneous catalyst it is 62.3% of total energy consumed in a process. Using a lower methanol to oil molar ratio at the same temperature and pressure of 280 °C and 28 MPa the apparent reaction rate constant will be significantly lower and it would be necessary to increase considerably the value of contact time in fixed bed reactor in order to reach 97% triglyceride's conversion. Such a large decrease of reaction rate of methanolysis could be suppressed using efficient heterogeneous catalyst. An addition of homogeneous catalyst is not appropriate since the unwanted side reaction of saponification would pick-up if vegetable oil contains a higher amount of free fatty acids. The second problem caused by the use of homogeneous catalyst is necessary step of FAME washing [68]. Another type of industrial reactor instead of the fixed bed reactor (e.g. the slurry reactor with smaller diameter of particles) would be more appropriate, among other reasons also due to the fact that heterogeneous catalyst must be separated from the reaction mixture by filtration.

The large amount of consumed energy in supercritical methanolysis comes from recovery of excess methanol from reaction mixture and its recycling into the process. Comparing energy consumption at the same pressure and temperature and with the same degree of conversion but with reduced methanol to oil

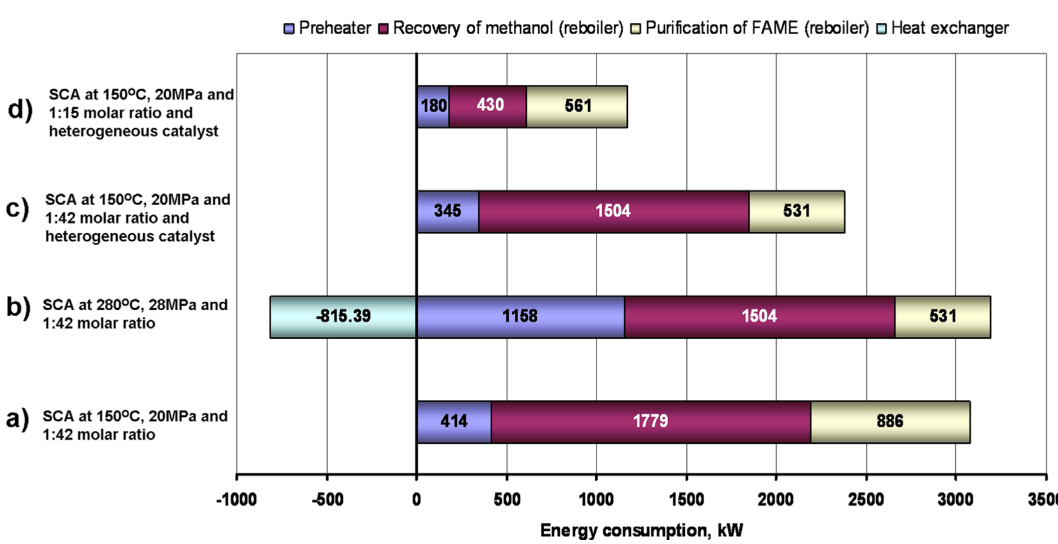


Fig. 6. Energy consumption for SCA applied at different process conditions (temperature, pressure, oil to methanol molar ratio and with or without use of heterogeneous catalyst).

molar ratio (from 42:1 to 15:1) shows that this would reduce the total energy consumption by 50% (Fig. 6c and d). However, the change of process conditions would also influence the energy needed for preheating of reaction mixture, as well as for pumping it to desired pressure.

Thus, it can be concluded that decrease of methanol to oil ratio from 42 to 20 would substantially reduce the necessary energy in reboiler of distillation column for methanol recycling (35% of total energy consumption in FAME synthesis).

From recently published data [6,9] it was found that biodiesel production at supercritical conditions (at 42:1 methanol oil molar ratio) requires the same amount of energy as a commercial process of FAME synthesis at lower temperature (80 °C and 6:1 methanol to oil molar ratio) based on alkali as catalyst (NaOH). Furthermore, the FAME synthesis based on use of heterogeneous catalyst followed by lower methanol to oil molar ratio from (e.g. from 12:1 to 20:1) and at moderate temperature and pressure would probably be the best solution for biodiesel production. Synthesis based on use of heterogeneous catalyst is not followed by undesired creation of waste water and other side products usually present during purification of FAME and glycerol in classical alkali process.

Although the energy cost is only 16% of total biodiesel production cost [87] the synthesis of FAME based on heterogeneous catalytic process could substantially reduce it (for almost 50%) and thus significantly decrease the total production cost. Moreover, the heterogeneous FAME synthesis could be also used with low cost feedstock containing a larger amount of free fatty acids which is not possible in the case of classical alkali catalyzed process. Also, economic assessment of biodiesel process using heterogeneous alkali catalyst (CaO) showed that such process has a lowest plant and manufacturing cost [87,88].

2.5. Application of heterogeneous catalyst for energy efficient process

Many types of heterogeneous catalysts, such as alkaline earth metal oxides, various alkaline metal compounds supported on alumina or zeolites can catalyze reactions of vegetable oil alcoholysis. Some of investigated catalysts like commercial hydrotalcite [99], zeolites and modified zeolites [100,101], Na/NaOH/γ-Al_2O_3 [102] are quite expensive or complicated to prepare, which limita their industrial application. Stern and co-authors developed zinc oxide, or a mixture of zinc oxide and alumina, or zinc aluminates as solid and methanol insoluble catalysts [103]. Alumina loaded with alkali metal salts (KI, KF, K_2NO_3 or K_2CO_3) or different potassium compounds were demonstrated as an efficient solid-base catalyst [104–107].

Many R&D focused on use of heterogeneous catalysts was based on their application at temperature and pressure similar to conventional HACA process (around 65 °C and methanol to oil moil ratio less than 9) [108–120]. Results of these investigations indicated that for a higher rate of methanolysis and decrease of reaction time for obtaining a high conversion of triglycerides the higher temperature and pressure must be applied (CaO and MgO) [121–126]. However, applied conditions of heterogeneously catalyzed FAME synthesis are very close to the supercritical conditions when reaction of methanolysis (SCA) can be also completed without the presence of any catalyst [68]. The most important parameter for the final decision regarding applicability of heterogeneous catalyst is determined by possibility for several reuses of the same amount of catalyst in a process without drastic decrease of catalyst activity as well its easy and complete separation from the final products (FAME and glycerol). Furthermore, the catalyst should be insoluble in supercritical or subcritical methanol and at same time being stable and without any reaction with some compound present in reaction mixture thus causing its deactivation. Unfortunately, for most supported alkali catalysts, the active ingredients are easily corroded by methanol and they exhibit short catalyst lifetimes and the main attention in future research should be pointed on that evidence taking into account the economic aspects of FAME synthesis as well as potential industrial applicability.

Moreover, the most important characteristic of heterogeneous catalyst for suggested biodiesel technology is its possibility to convert the feedstock with high amount of FFA. Since now, there is only two type of homogenous base catalyst which could convert FFA easily. As recently reported CaO supported by metals as Li is a promising heterogeneous catalyst for biodiesel synthesis and activity of such modified CaO catalyst was not significantly affected by the presence of a high FFA content (up to 5.75%) indicating that same reaction time is necessary for obtaining defined conversion of triglycerides [127,128]. Recently, the group of authors [129] reported that lanthanum modified CaO catalyst can be directly utilized on waste or unrefined oils (up to 3.6 mass% of FFA and 10 mass% of water).

The main important limitation for industrial application of heterogeneous process of biodiesel production could be the cost and lifetime of catalyst as well as its separation from reaction mixture. FAME synthesis in a plug flow reactor where effective solid catalyst is arranged as packed-bed used for a longer period of time is the best solution which could be applied on industrial scale.

This and some other working conditions (temperature and pressure, supercritical or subcritical conditions) as well as the phase′s behavior of complex reaction mixture could be limiting steps for improved efficiency of FAME synthesis and should be the main task of future research. Also, the development of highly efficient heterogeneous catalyst, which can convert the feedstock with high levels of FFA and water content, will be important task of future research.

3. Techno-economic analysis

Nowadays, biodiesel is well accepted as a renewable energy carrier. However, a high production cost of biodiesel, mainly the price of vegetable oil (rapeseed, sunflower, soybean, etc.) is still remaining a problem. Since now there are some results of analysis recently published in literature which analyze and give good prediction for biodiesel production price [130–151].

Bender [131] reviewed 12 studies, involving several feedstocks and operational scales, of the economic feasibility of biodiesel production. Calculated production costs (which included the cost of the feedstock and its conversion to biodiesel) ranged from US $0.30/L for fuel produced from soybeans to US $0.69/L when rapeseed was the feedstock. These estimates were based on biodiesel production as a part of integrated oilseed crushing and processing plant, and thus the use of oilseeds as the starting material and market value of the meal co-product was included into the cost of the biodiesel. When an oilseed processing facility is not included, it may be necessary for a biodiesel operation to use existing feedstock with its actual price on the market. Thus, using an estimated process cost of US $0.16/L for biodiesel production, and estimating a feedstock cost of US$0.54/L for refined soy oil, an overall cost of US $0.70/L for the production of soy-based biodiesel was estimated [132]. Details regarding the chemical processes or the production facility used to draft this estimate were not provided. Canacki and Van Gerpen [133] reported a production cost, exclusive of feedstock expense, of US $0.42/L for biodiesel produced from refined, bleached and deodorized soy oil in a small pilot scale plant (190 L, batch process). These authors did not include revenue from the sale of glycerol, and did not estimate or

include the capital costs in their calculation. Graboski and McCormick [134] summarized a model for the production of 37.8 million litres (10 million galons) of biodiesel annually, concluding that the joint cost of feedstock and of its conversion to biodiesel would be US $0.57/L. Note that in all the cases cited above, the feedstock cost comprises a very substantial portion of overall biodiesel cost (around 70–80%) [131–151]. This highlights the need for development of applicable technology which could be effective if lower value feedstock is applied.

Zhang et al. [77] developed a HYSYS-based process simulation model to assess the technological feasibility of four biodiesel plant configurations – a homogeneous alkali-catalyzed pure vegetable oil process; a two step process to treat waste vegetable oil; a single step homogeneous acid-catalyzed process to treat waste vegetable oil; and a homogeneous acid-catalyzed process using hexane extraction to help purify the biodiesel. All four configurations were deemed technologically feasible, but a subsequent economic analysis of the four designs revealed that the one step acid-catalyzed process was the most economically attractive [94]. Haas et al. [89] developed a versatile process simulation model to estimate biodiesel production costs; however, the model was limited to a traditional alkali-catalyzed production method.

The economic analysis for supercritical alcoholysis of waste oil (SCA) was performed by Glisic and Skala [6] using methodology proposed by Peters, Timmerhaus and West [152] and consulting the chemical process design handbooks [153–155] (10.000 t/year of biodiesel production; 7900 working hours). The cost of SCA process from this analysis was compared to the cost of conventional biodiesel plant (HACA). The equipment cost is corrected with the CEPCI ratio (Chemical engineering's Plant Cost Index) which was for the January 2002 390.3 and for the August 2008, 619.3. The equipment cost of HACA process was obtained from data of Van Gerpen [140] based on analysis of FFA present in feedstock on installed cost of biodiesel plant. The raw materials for biodiesel synthesis in booth analyzed cases (SCA and HACA) assume that the waste vegetable oil (feedstock) contains 5% of FFA. The total installed cost (total capital investment) includes the direct and indirect costs and working capital, and it is shown in Table 6.

Table 6
Total capital investment for analyzed processes (in million US$) [6].

Direct Costs	Process	
	SCA	HACA
Purchased equipment	**0.892**	**0.920**
Delivery	0.089	0.090
Purchased equipment installation	0.461	0.480
Instrumentation & Controls (installed)	0.353	0.360
Piping (installed)	0.667	0.690
Electrical systems (installed)	0.108	0.110
Buildings (including services)	0.177	0.180
Yard improvements	0.098	0.100
Service facilities (installed)	0.687	0.710
Total direct costs	**3.533**	**3.640**
Indirect Costs		
Engineering and supervision	0.324	0.330
Construction expenses	0.402	0.410
Legal expenses	0.039	0.040
Contractor's fee	0.216	0.220
Contingency	0.432	0.450
Total indirect costs	**1.413**	**1.460**
Fixed capital investment	**4.946**	**5.100**
Working capital	**0.873**	**0.901**
TOTAL CAPITAL INVESTMENT	**5.819**	**6.001**

Table 7
Annual total product cost at 100% capacity (million US$) [6].

Item	Process	
	SCA	HACA
Raw materials	2.913	3.044
Operating labor	1.051	1.226
Operating supervision	0.158	0.184
Utilities	0.607	0.853
Maintenance and repairs	0.297	0.306
Operating supplies	0.045	0.046
Laboratory charges	0.158	0.184
Royalties	0.073	0.082
Variable cost	**5.300**	**5.925**
Taxes (property)	0.099	0.102
Insurance	0.049	0.051
Plant overhead, general	0.903	1.030
Manufacturing cost	**6.352**	**7.108**
Administration	0.301	0.343
Distribution & sales	0.366	0.409
Research & Development	0.292	0.328
General expenses	0.959	1.080
Total product cost without depreciation	**7.311**	**8.188**
ROI, average %/year	8.500	8.500
Pay back period, year	5.000	5.000
Biodiesel price without taxes, US$	**0.94**	**1.04**

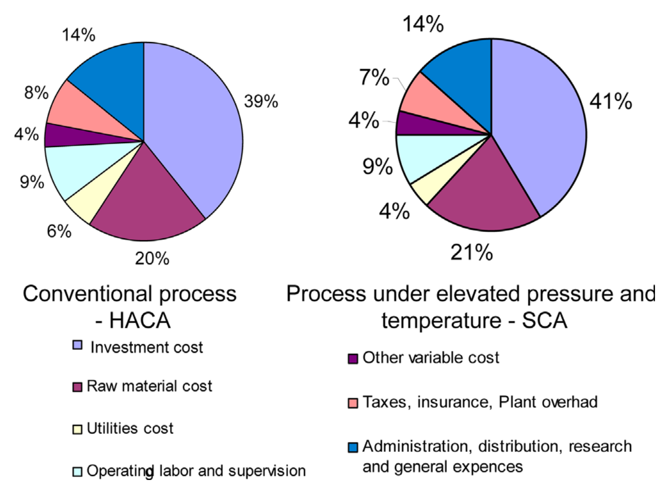


Fig. 7. The analysis of impact of different costs to total product cost.

The obtained results showed that almost the same value of capital investment is needed for SCA and HACA process (5.819 and 6.001 million US$ for 10.000 t/year of biodiesel production capacity). This conclusion was contradictory to the widely spread belief that such high pressure and temperature technology would require excessively high capital investment for biodiesel production. The annual total product cost at 100% capacity including taxes, insurance, and plant overhead, as well as manufacturing cost (administration, distribution and selling, research and development, general expenses) is shown in Table 7.

The specific analysis of total annual production cost and the installed cost of biodiesel plant for analyzed cases as well as those already published in literature is shown in Fig. 7. Evidently, the energy cost does not play an important role in the total product cost and the price of final product (biodiesel) mainly depends on raw material (vegetable oil) cost. The cost of energy represents only 4% while the cost of waste oil and methanol constitutes 21% of the total annual production cost. This comparison indicates that investment cost is also very important as it constitutes 41% of total

annual product cost. Similar results were obtained by the other authors [86].

Very important conclusion based on this analysis is that the conventional technology of FAME synthesis (HACA) based on the use of feedstock with higher FFA concentration (5%) requires higher capital investment, while the amount of consumed energy is equal to the energy consumed by SCA. Finally a detailed analysis of biodiesel production cost produced by HACA process is higher by 11% than for biodiesel produced using SCA. It is important to notice that although similar percentage of different costs in total product cost was obtained; the reported biodiesel production cost is remarkably different [6].

Performed analysis also indicates that future "optimal" capacity of biodiesel industrial unit based on SCA technology is very important and this question needs very fine and sensitive analysis. It is well known that the total investment cost could be related to capacity using power of 0.6–0.8, while the prices of raw materials as well as utilities increase almost linearly with capacity. Such relation between different costs will change percentages shown in Fig. 7.

Also, overall production cost and profitability, to certain extent, depend on the price of glycerol. Ever increasing production volume of biodiesel has also increased amount of glycerol on the market. The production of glycerol in the World is going through historical peak and continues to increase year after year. In year 2003 glycerol prices were around $1200 per tone, while current prices are estimated around $450–550 per tone, depending on the purity and location, and still falling down. The value of crude glycerol has also dropped and recent prices in the US are quoted at $0–$70 per tone. Most biodiesel producers attach zero value to the crude glycerol. Crude glycerol can be assumed to have a negative value in the close future. Huge oversupply is placing the producers of biodiesel in a situation where it is not possible to sell glycerol as a valuable feedstock for cosmetic and pharmaceutical industry. Instead of turning this asset into revenue they even have to pay for transport which is net addition to the overall production cost. This means that future successful operation of industrial plant for biodiesel production will require acceptable and profit driven use of glycerol for different purposes.

4. Conclusion

Biodiesel production under supercritical conditions of methanol or ethanol (SCA) is a promising and competitive technology when compared to conventional homogeneous alkali catalyzed alcoholysis (HACA). Also, SCA biodiesel production technology has significant advantages regarding environment protection since SCA is not followed by generation of waste water after purification of final products, which is the case of conventional HACA process. SCA yields almost pure products (FAME or FAEE and glycerol) which can be easily separated in the final stage of synthesis.

Furthermore, SCA can be easily applied for converting the feedstock with a higher content of free fatty acids, i.e. the low cost feedstock, which is not possible with conventional HACA process. That point has significant influence on the biodiesel price, biodiversity issues and on the current food or fuel dilemma.

The most important parameter affecting production cost for supercritical or subcritical alcoholysis is process energy consumption. Energy consumption mainly depends on the conversion of triglycerides, and could be almost 25% lower at supercritical alcoholysis if conversion is increased from 97 mass% to 100 mass %. Substantial decrease of energy consumption could be achieved at subcritical conditions only if methanol to oil molar ratio is reduced from 42:1 to 15:1, but such working conditions require the use of effective heterogeneous catalyst.

Very important conclusion based on techno-economic analysis is that the conventional technology of FAME synthesis (HACA) based on the use of feedstock with higher FFA concentration (5%) requires higher capital investment, while the amount of consumed energy is equal to the energy consumed by SCA. Biodiesel production cost using HACA process is higher by 11% than for biodiesel produced using SCA. Performed analysis also indicates that future "optimal" capacity of biodiesel industrial unit based on SCA technology is very important and this question needs very detailed and sensitive analysis.

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